STATEMENT

I, Yukio KAWAHARA—of ARK Mori Building, 13F, 12-32, Akasaka 1-chome, Minato-ku, Tokyo 107-6013 Japan—hereby declare that I am conversant in both Japanese and English and that I believe the following is true and correct translation of Japanese Patent Application No. 11-304847.

Date: May 18, 2004

Yukio KAWAHARA

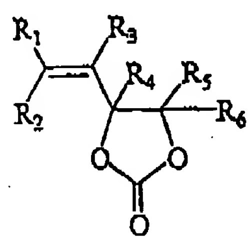
[Designation of Document] Specification

[Title of the Invention] Non-aqueous electrolyte secondary battery

[Claims]

1. A non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode, and a non-aqueous electrolyte comprising a solute and a non-aqueous solvent, characterized in that said non-aqueous solvent contains one or two or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the following general formula (I) incorporated therein:

[Ka 1]



(I)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

2. The non-aqueous electrolyte secondary battery according to Claim 1, characterized in that said

non-aqueous solvent comprises at least one vinylethylene carbonate represented by said general formula (I) incorporated therein, and has a relative dielectric constant of not smaller than 25.

3. The non-aqueous electrolyte secondary battery according to Claim 1 or 2, characterized in that an amount of the comprised vinylethylene carbonate compounds represented by said general formula (I) is 0.01 to 10% by weight of the sum of said non-aqueous solvent and said vinylethylene carbonate compounds represented by said general formula (I)

4. The non-aqueous electrolyte secondary battery according to anyone of Claims 1 to 3, characterized in that said non-aqueous solvents having a relative dielectric constant of not smaller than 25 is anyone of solvents selected from the group consisting of ethylene carbonate, propylene carbonate, butylene carbonate, γ-butyrolactone and γ-valerolactone.

5. The non-aqueous electrolyte secondary battery according to anyone of Claims 1 to 4, characterized in that said negative electrode contains a carbon-based material capable of absorbing and releasing lithium.

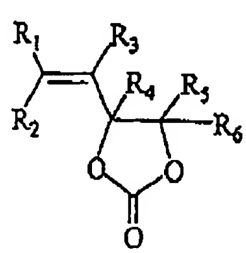
6. The non-aqueous electrolyte secondary battery according to anyone of Claims 1 to 5, characterized in that said negative electrode is a carbon-based material

capable of absorbing and releasing lithium or a mixture of one or more material selected from said carbon-based material, lithium and an lithium ally, and a metal oxide capable of absorbing and releasing lithium.

7. The non-aqueous electrolyte secondary battery according to Claim 5 or 6, characterized in that said carbon-based material comprises graphite having a d value of from 0.335 to 0.340 nm on lattice plane (002 plane) as determined by X-ray diffractometry.

8. A non-aqueous electrolyte for a non-aqueous electrolyte secondary battery comprising at least a negative electrode and a positive electrode capable of absorbing/releasing lithium which comprises a solute and a non-aqueous solvent, characterized in that said non-aqueous solvent contains one or two or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the following general formula (I) incorporated therein:

[Ka 2]



(I)

wherein R^1, R^2, R^3, R^4, R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

[Detailed Description of the Invention]

[0001]

[Technical Field to which the Invention Belongs]

The present invention relates to a non-aqueous electrolyte secondary battery and a non-aqueous electrolyte used therefore. More particularly, the present invention relates to an improvement in a non-aqueous electrolyte secondary battery comprising an electrolyte containing a vinylethylene carbonate compound having a specified structure incorporated therein.

According to the present invention, can be provided a secondary battery using a non-aqueous solvent having a high relative dielectric constant which has a high charge and discharge efficiency, an excellent cycle performance and a high safety.

[0002]

[Prior Art]

With the recent trend for the reduction of weight and size of electrical appliances, there has been a growing demand for lithium secondary battery having a high energy

density. Further, with the expansion of the field to which the lithium Secondary battery can be applied, it has been desired to further improve the battery performance.

Extensive studies have been heretofore made of secondary battery comprising metallic lithium as a negative electrode as battery which can attain a high capacity. However, the greatest technical problem that prevents the practical use of such a secondary battery was that when charge and discharge are repeated, metallic lithium grows in the form of dendrite and eventually reaches the positive electrode, causing shortcircuiting in the battery.

[0003]

To cope with this problem, a non-aqueous electrolyte secondary battery comprising as a negative electrode a carbon-based material capable of absorbing/releasing lithium ion such as coke, artificial graphite and natural graphite has been proposed. In such a non-aqueous electrolyte secondary battery, lithium doesn't exist in metallic state, making it possible to inhibit the formation of dendrite and improve the battery life and safety. In particular, a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material such as artificial graphite and natural graphite has been noted as one meeting the demand for higher

capacity.

[0004]

In a lithium secondary battery comprising the foregoing carbon-based material, as a solvent having a high dielectric constant of a non-aqueous electrolyte, generally, cyclic carbonates such as propylene carbonate and ethylene carbonate are widely used. While in a non-aqueous electrolyte secondary battery comprising a non-graphite carbon-based material such as coke, a solvent containing propylene carbonate can be suitably used. Further, in a non-aqueous electrolyte secondary battery comprising as a negative electrode a graphite carbon-based electrode material, singly or in admixture with other negative electrode materials capable of absorbing and releasing lithium, if a solvent comprising propylene carbonate is used, the decomposition of propylene carbonate proceeds violently on the surface of the electrode during charging, disabling the smooth absorption of lithium into the graphite electrode and smooth release of lithium from the graphite electrode.

[0005]

On the other hand, ethylene carbonate undergoes little such decomposition and thus has been widely used as a solvent having a high dielectric constant of an electrolyte for a non-aqueous electrolyte secondary

battery comprising a graphite negative electrode. However, even if ethylene carbonate is used as a solvent, it cannot sufficiently suppress such problem that the electrolyte decomposes to cause deterioration of cycle performance, etc. Further, ethylene carbonate exhibits a solidifying point as high as 36.4°C as compared with propylene carbonate and thus is not used singly but is used normally in admixture with a low viscosity solvent. For this reason, the electrolyte for a lithium secondary battery comprising a graphite-based negative electrode normally comprises a mixture of ethylene carbonate and diethyl carbonate. However, since most such low viscosity solvents normally have a low boiling point, it is disadvantageous in that when added in a large amount, the solvent exhibits a lowered flash point, though giving good electrolyte properties. On the contrary, when added only in a small amount, it is disadvantageous in electrical conductivity and viscosity at low temperatures.

[0006]

Under these circumstances, Japanese Patent Laid-Open No. 1992-87156 proposes, in a non-aqueous electrolyte battery comprising as a negative electrode lithium, an electrolyte comprising as a solvent a compound of which chain has unsaturated carbon-carbon bond difficultly reactive with lithium, e.g., vinylethylene

carbonate. However, vinylethylene carbonate is used as a mixture with 1,2-dimethoxyethane which is a low boiling solvent in the same volume and, therefore, cannot solve the foregoing problem.

[0007]

On the other hand, γ-butyrolactone, etc., which is a cyclic ester, has a high relative dielectric constant as well as a low solidifying point and thus can be used without being mixed with a low viscosity solvent. However, the γ-butyrolactone-based electrolyte, too, is subject to progress of decomposition of γ-butyrolactone on the surface of the graphite electrode during charge, causing deterioration of battery performance.

Japanese Patent Laid-Open No. 1999-31525 proposes an electrolyte solvent comprising as a main component γ-butyrolactone and as a subsidiary component ethylene carbonate in an amount of from 15 to 35% by volume and practically comprising diethyl carbonate in an amount of not smaller than 16% by volume to inhibit the decomposition of γ-butyrolactone in a non-aqueous electrolyte secondary battery comprising a graphite-based carbon material as a negative electrode.

[0008]

[Problems that the Invention is to Solve]

However, the electrolytes disclosed as a known

technique leave something to be improved, though showing an excellent effect in its own way. An object of the present invention is to provide a non-aqueous electrolyte secondary battery which can exhibit a desirable battery performance even in case of using a non-aqueous solvent having a relatively high flash point and a relative dielectric constant of not smaller than 25 as a main solvent.

[0009]

[Means for Solving the Problems]

Under these circumstances, the inventors made extensive studies. As a result, it was found that as a solvent of an electrolyte of a non-aqueous electrolyte secondary battery, the use of a non-aqueous solvent comprising one or two more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight and exhibiting a flash point of not lower than 70°C to which at least one vinylethylene carbonate having a specified structure is added can provide a non-aqueous electrolyte secondary battery having a high charge discharge efficiency, an excellent cycle performance and safety. The present invention has thus been worked out.

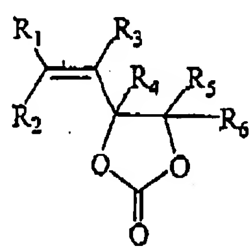
[0010]

In other words, the essence of the invention lies

in a non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode, and a non-aqueous electrolyte comprising a solute and a non-aqueous solvent, characterized in that the non-aqueous solvent contains one or two or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one vinylethylene carbonate represented by the following general formula (I) incorporated therein:

[0011]

[Ka 3]



(I)

[0012]

wherein R^1, R^2, R^3, R^4, R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms as well as a non-aqueous electrolyte using for the battery.

It should be noted that the non-aqueous solvent to be used in the secondary battery of the present invention preferably contains one or two or more solvents selected

from solvents having a relative dielectric constant of not smaller than 25 and at least one kind of a vinylethylene carbonate compound represented by the foregoing general formula (I).

[0013]

The amount of the added vinylethylene carbonate compound represented by the foregoing general formula (I) is preferably 0.01 to 10% by weight of the sum of the non-aqueous solvent and the vinylethylene carbonate compound represented by the general formula (I).

The negative electrode to be used in the secondary battery of the present invention preferably contains a carbon-based material capable of absorbing and releasing lithium.

[0014]

[Mode for Carrying Out the Invention]

A non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode, and a non-aqueous electrolyte comprising a solute and a non-aqueous solvent of the present invention is characterized in that the non-aqueous solvent contains one or two or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least

one vinylethylene carbonate represented by the foregoing general formula (I) incorporated therein.

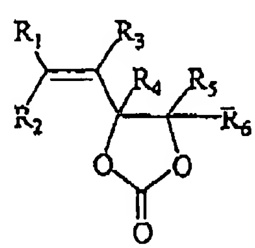
[0015]

The non-aqueous solvent having a relative dielectric constant of not smaller than 25 to be used in the present invention is not specifically limited. However, ethylene carbonate, propylene carbonate, butylenes carbonate, γ-butyrolactone, γ-valerolatone, sulfolane, 3-methylsulfolane, dimethyl sulfoxide, etc. can be exemplified. Preferred among these non-aqueous solvents are ethylene carbonate, propylene carbonate, γ-butyrolactone, and γ-valerolatone. Two or more of these solvents may be used in admixture. The combination of these solvents is not specifically limited.

To the non-aqueous solvent to be used in the present invention is added vinylethylene carbonate represented by the following general formula (I):

[0016]

[Ka 4]



(I)

[0017]

wherein R^1, R^2, R^3, R^4, R^5 and R^6 each independently represent a hydrogen atom or an alkyl group having 1 to 4 carbon atoms.

When R^1, R^2, R^3, R^4, R^5 and R^6 are alkyl groups having 1 to 4 carbon atoms, specific examples thereof include methyl group, ethyl group, n-propyl group, i-propyl group, n-butyl group, sec-butyl group, and tert-butyl group. Preferred among these alkyl groups are methyl group and ethyl group.

[0018]

Specific examples of the vinylethylene carbonate compound represented by the general formula (I) include 4-ethenyl-1,3-dioxolane-2-one (occasionally referred to as "vinylethylene carbonate"),

4-ethenyl-4-methyl-1,3-dioxolane-2-one,

4-ethenyl-4-ethyl-1,3-dioxolane-2-one,

4-ethenyl-4-n-propyl-1,3-dioxolane-2-one,

4-ethenyl-5-methyl-1,3-dioxolane-2-one,

4-ethenyl-5-ethyl-1,3-dioxolane-2-one,

4-ethenyl-5-n-propyl-1,3-dioxolane-2-one, etc.

[0019]

In particular, vinylethylene carbonate, 4-ethenyl-4-methyl-1,3-dioxolane-2-one are preferred, and vinylethylene carbonate is particularly preferred.

They can be used in any mixture thereof.

An amount of vinylethylene carbonate of the general formula (I) to be added in the present invention is normally from 0.01 to 10% by weight, preferably from 0.1 to 10% by weight, more preferably from 0.5 to 7% by weight.

[0020]

In a non-aqueous solvent to be used in the present invention, a solvent having a relative dielectric constant of not smaller than 25 is included in an amount of not smaller than 90% by weight. In the present invention, the non-aqueous solvent preferably comprises the foregoing solvent having a relative dielectric constant of not smaller than 25 and vinylethylene carbonate represented by the foregoing general formula (I) incorporated therein.

Further, in the present invention, to the non-aqueous solvent having a relative dielectric constant of not smaller than 25 may be added one or more non-aqueous solvents other than those as mentioned above, e.g., dialkyl (preferably having from 1 to 4 carbon atoms) carbonates such as dimethyl carbonate, diethyl carbonate, di-n-propyl carbonate and ethylmethyl carbonate, cyclic ethers such as tetrahydrofuran and 2-methyltetrahydrofuran, chain ethers such as dimethoxyethane and dimethoxymethane, chain esters such

as methyl acetate and ethyl propionate. In this case, these solvents may be added in such a combination that the flash point of the non-aqueous solvents, including those added, is not lower than 70°C.

[0021]

As the solute of the electrolyte to be used in the invention there may be used a lithium salt. The usable lithium salt is not specifically limited so far as it can be used as a solute of an electrolyte. For example, an inorganic lithium Salt selected from $LiClO_4$, $LiPF_6$ and $LiBF_4$ or a fluorine-containing organic lithium salt such as $LiCF_3SO_3$, $LiN(CF_3SO_2)_2$, $LiN(CF_3CF_2SO_2)_2$, $LiN(CF_3SO_2)(C_4F_9SO_2)$ and $LiC(CF_3SO_2)_3$ can be used. Preferred among these lithium salts are $LiPF_6$ and $LiBF_4$. Two or more of these lithium salts may be used in admixture.

[0022]

The molar concentration of a lithium salt as a solute in the electrolyte is normally from 0.5 to 2.0 mols/l. When the molar concentration of the lithium salt falls below 0.5 mols/l or exceeds 2.0 mols/l, it is disadvantageous in that the electrolyte exhibits a low electrical conductivity that is liable to cause deterioration of the battery performance.

The material of the negative electrode constituting the battery of the present invention is preferably one

containing a carbon-based material capable of absorbing and releasing lithium. Specific examples of such a carbon-based material include pyrolysis products of organic materials obtained under various pyrolysis conditions, artificial graphite, natural graphite, etc. Preferably, artificial graphite produced by high temperature heat treatment of graphitizable pitch obtained from various raw materials, other artificial graphite such as graphitized mesophase globule and graphitized mesophase pitch-based carbon fiber, purified natural graphite or materials obtained by subjecting these graphites to various surface treatment including pitch may be used.

[0023]

However, these carbon-based materials preferably have a d value (interlaminar distance) of from 0.335 to 0.34 nm, more preferably from 0.335 to 0.337 nm on lattice plate (002 plane) determined by X-ray diffractometry. These carbon-based materials preferably have an ash content of not greater than 1% by weight, more preferably not greater than 0.5% by weight, most preferably not greater than 0.1% by weight, and a crystalline size (Lc) of not smaller than 30 nm as determined by X-ray diffractometry according to the method of the Japan Society of Promotion of Scientific Research. Further,

the crystalline size of the carbon-based materials is more preferably not smaller than 50 nm, particularly preferably not smaller than 100 nm.

[0024]

The median diameter of a carbon-based material is preferably from 1 to 100 μm, more preferably from 3 to 50 μm, further preferably from 5 to 40 μm, particularly preferably from 7 to 30 μm as determined by laser diffractometry/scattering method. BET process specific surface area of the carbon-based material is preferably from 0.3 to 25.0 m^2/g, more preferably from 0.5 to 20.0 m^2/g, even more preferably from 0.7 to 15.0 m^2/g, particularly preferably from 0.8 to 10.0 m^2/g. An intensity ratio of peak P_A (peak intensity I_A) in the range of from 1,580 to 1,620 cm^{-1} and peak P_B (peak intensity I_B) in the range of from 1,350 to 1,370 cm^{-1} determined by Raman spectroscopy using argon ion laser: R (= I_B/I_A) is preferably 0 to 1.2 and a peak half width is preferably 26 cm^{-1} or less, particularly preferably 25 cm^{-1} or less in the range of from 1,580 to 1,620 cm^{-1}.

[0025]

Further, the carbon-based material may be used by further mixing a negative electrode material capable of absorbing and releasing lithium therewith. Examples of the negative electrode material capable of absorbing and

releasing lithium other than the carbon-based material include metal oxide materials such as tin oxide and silicon oxide, metallic lithium, and various lithium alloys. Two or more of these negative electrode materials may be used in admixture.

The process for the production of a negative electrode from these negative electrode materials is not specifically limited. The negative electrode can be produced, e.g., by optionally adding a binder, a thickening agent, an electrically-conducting material, a solvent, etc. to a negative electrode material to make a slurry, applying the slurry to a current collector substrate, and then drying the coated substrate. Alternatively, the negative electrode material may be rolled as it is to prepare a sheet-like electrode or may be compression-molded to prepare a pelletized electrode.

[0026]

The binder to be used in the production of the electrode is not specifically limited so far as it is a material inert to the solvent to be used in the production of the electrode or the electrolyte. Specific examples of such a material include polyvinylidene fluoride, polytetrafluoroethylene, styrene-butadiene rubber, isoprene rubber, butadiene rubber, etc.

Examples of the thickening agent include

carboxymethyl cellulose, methyl cellulose, hydroxymethyl cellulose, ethyl cellulose, polyvinyl alcohol, oxidized starch, phosphated starch, casein, etc.

Examples of the electrically-conducting material include metallic materials such as copper and nickel, and carbon-based materials such as graphite and carbon black.

As the material of the current collector for a negative electrode there may be used metals such as copper, nickel and stainless steel. Preferred among these metals is a copper foil because it can be easily formed into a thin film and from the Stand point of cost.

[0027]

As the material of the positive electrode constituting the battery of the present invention there may be used a material capable of absorbing and releasing lithium such as a lithium transition metal composite oxide material, e.g., lithium cobalt oxide, lithium nickel oxide and lithium manganese oxide.

The process for the production of the positive electrode is not specifically limited. The positive electrode can be produced according to the foregoing process for the production of the negative electrode. Referring to the shape of the positive electrode, a binder, an electrically-conducting material, a solvent, etc. may

be optionally added to and mixed with the positive electrode material and the resulting mixture is then applied to a current collector substrate to form a sheet electrode or press-molded to form a pelletized electrode.

As the material of the current collector for positive electrode there may be used a metal such as aluminum, titanium and tantalum or alloy thereof. Particularly preferred among these materials is aluminum or alloy thereof because it has a light weight and thus gives a high energy density.

[0028]

The material and shape of the separator to be used in the battery of the present invention are not specifically limited.

However, the separator is preferably selected from materials which are inert to the electrolyte and have excellent liquid retaining properties. A porous sheet or nonwoven cloth made of a polyolefin such as polyethylene and polypropylene as a raw material is preferably used.

[0029]

The process for the production of the battery of the present invention having at least a negative electrode, a positive electrode and a non-aqueous electrolyte is not specifically limited but can be properly selected from those commonly employed.

The shape of the battery is not specifically limited. A cylinder type obtained by spirally winding a sheet-like electrode and a separator, a cylinder type having an inside out structure comprising a pelletized electrode and a separator in combination, a coin type having a pelletized electrode and a separator laminated on each other, etc. can be used.

[0030]

[Examples]

The present invention will be further described in the following examples and comparative examples, but the present invention should not be construed as being limited thereto so far as they fall within the scope of the invention.

EXAMPLE 1

To 85 parts by weight of $LiCoO_2$ as a positive active material were added 6 parts by weight of carbon black, 9 parts by weight of a polyvinylidene fluoride KF-1000 (trade name; produced by Kureha Chemical Industry Co., Ltd.), followed by mixing. The mixture obtained was then dispersed with N-methyl-2-pyrrolidone to make a slurry. The slurry was uniformly applied to an aluminum foil having a thickness of 20 μm as a positive electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a positive electrode.

[0031]

To 95 parts by weight of KS-44 (trade name; produced by Timcal Co., Ltd.), which is an artificial graphite powder having a d value of 0.336 nm on lattice plane (002 plane) as determined by X-ray diffractometry, a crystalline size (Lc) of not lower than 100 nm (264 nm), an ash content of 0.04% by weight, a median diameter of 17 μm as determined by laser diffractometry/scattering method, a BET process specific surface area of 8.9 m^2/g, an intensity ration of peak P_A (peak intensity I_A) in the range of from 1,580 to 1,620 cm^{-1} and peak P_B (peak intensity I_B) in the range of from 1,350 to 1,370 cm^{-1} determined by Raman spectroscopy using argon ion laser: R (= I_B/I_A) of 0.15 and a peak half width of 22.2 cm^{-1} in the range of from 1,580 to 1,620 cm^{-1} as a negative active material were added 5 parts by weight of polyvinylidene fluoride. The resulting mixture was then dispersed with N-methyl-2-pyrrolidone to make a slurry. The slurry thus made was uniformly applied to a copper foil having a thickness of 18 μm as a negative electrode current collector, dried, and then punched into a disk having a diameter of 12.5 mm to prepare a negative electrode.

[0032]

An electrolyte was prepared by dissolving vinylethylene carbonate in a 1 : 1 (by volume) mixture

of propylene carbonate and ethylene carbonate in a proportion of 3% by weight per 97% by weight, and then dissolving thoroughly dried lithium hexafluorophosphate ($LiPF_6$) as a solute in the solution in an amount of 1 mol/l in dried argon atmosphere.

The positive electrode was then received in a stainless steel can which also acts as a positive electrode conductor.

The negative electrode was then put on the positive electrode with a polyethylene separator impregnated with the electrolyte interposed therebetween. The can was then caulked with a sealing plate which also acts as a negative electrode conductor with an insulating gasket interposed therebetween to seal the can. Thus, a coin type battery was prepared.

[0033]

COMPARATIVE EXAMPLE 1

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving $LiPF_6$ in a 1 : 1 mixture (by volume) of propylene carbonate and ethylene carbonate in an amount of 1 mol/l was used.

[0034]

EXAMPLE 2

A coin type battery was prepared in the same manner

as in Example 1 except that an electrolyte prepared by dissolving vinylethylene carbonate in a 1 : 1 mixture (by volume) of ethylene carbonate and γ-butyrolactone in a proportion of 3% by weight per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0035]

COMPARATIVE EXAMPLE 2

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving $LiPF_6$ in a 1 : 1 mixture (by volume) of ethylene carbonate and γ-butyrolactone in an amount of 1 mol/l was used.

[0036]

EXAMPLE 3

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and γ-butyrolactone in a proportion of 3% by weight per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0037]

COMPARATIVE EXAMPLE 3

A coin type battery was prepared in the same manner

as in Example 1 except that an electrolyte prepared by dissolving $LiPF_6$ in a 1 : 1 mixture (by volume) of propylene carbonate and γ-butyrolactone in an amount of 1 mol/l was used.

[0038]

EXAMPLE 4

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving vinylethylene carbonate in propylene carbonate in a proportion of 3% by weight per 97% by weight, and then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

[0039]

COMPARATIVE EXAMPLE 4

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving $LiPF_6$ in propylene carbonate in an amount of 1 mol/l was used.

[0040]

EXAMPLE 5

A coin type battery was prepared in the same manner as in Example 1 except that an electrolyte prepared by dissolving vinylethylene carbonate in a 1 : 1 mixture (by volume) of propylene carbonate and ethylene carbonate in a proportion of 5% by weight per 95% by weight, and

then dissolving $LiPF_6$ in the solution in an amount of 1 mol/l was used.

The batteries prepared in Examples 1 to 5 and Comparative Examples 1 to 4 were then subjected to a charge-discharge test involving charge with a constant current of 0.5 mA to a termination voltage of 4.2 V and discharge to a termination voltage of 2.5 V at 25°C.

[0041]

The electrical conductivity of the electrolytes used in Examples 1 to 5 at 20°C and -30°C are set forth in Table 1. For the measurement of electrical conductivity, an electrical conductivity meter (CM-30S, produced by DKK-TOA CORPORATION) was used.

The flash point was measured according to JIS K-2265.

The discharge capacity per weight of negative electrode and charge-discharge efficiency at the 1st cycle of the various batteries are set forth in Table 2. The charge-discharge efficiency was determined by the following equation.

[0042]

[Formula 1]

Charge-discharge efficiency (%) = [(Discharge capacity)/(Charge capacity)] x 100

[0043]

As shown in Tables 1 and 2, Comparative Examples

1, 3 and 4 underwent violent decomposition of an electrolyte and thus didn't act as battery.

On the other hand, the electrolytes of the examples of the present invention didn't solidify even at -30°C and exhibit a relatively high conductivity and thus provide an excellent capacity and charge-discharge efficiency when used in battery.

[0044]

Table 1

Table 1

	Electrical conductivity (mS/cm)		Flash point °C
	20°C	-30°C	
Example 1	6.2	1.1	140
Example 2	9.1	2.6	119
Example 3	8.1	2.3	119
Example 4	5.3	1.0	138
Example 5	6.1	1.0	140

[0045]

[Table 2]

Table 2

	Capacity at 1st cycle (mAh/g)	Efficiency at 1st cycle (%)
Example 1	226	81.3
Example 2	230	83.0
Example 3	213	81.1
Example 4	198	78.1
Example 5	233	84.4
Comparative Ex.1	-	-
Comparative Ex.2	120	34.4
Comparative Ex.3	-	-
Comparative Ex.4	-	-

[0046]

[Effect of the Invention]

The non-aqueous electrolyte secondary battery of the present invention comprises a non-aqueous solvent comprising one or two more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight and exhibiting a flash point of not lower than 70°C and, therefore, has a high safety, a high charge discharge efficiency, and an excellent cycle performance. Further, in accordance with the present invention, can be produced a secondary battery having an excellent cycle performance

and storage properties even at high temperatures.

[Designation of Document] Abstract

[Abstract]

[Problem] To provide a non-aqueous electrolyte secondary battery comprising a non-aqueous solvent having a relatively high flash point and a relative dielectric constant of not smaller than 25 as a main solvent and having an excellent battery performance.

[Means for Resolution] A non-aqueous electrolyte secondary battery comprising at least a negative electrode, a positive electrode, and a non-aqueous electrolyte comprising a solute and a non-aqueous solvent, characterized in that the non-aqueous solvent contains one or more solvents selected from solvents having a relative dielectric constant of not smaller than 25 in an amount of not smaller than 90% by weight, exhibits a flash point of not lower than 70°C and comprises at least one

vinylethylene carbonate incorporated therein.

[Selected Drawing] none